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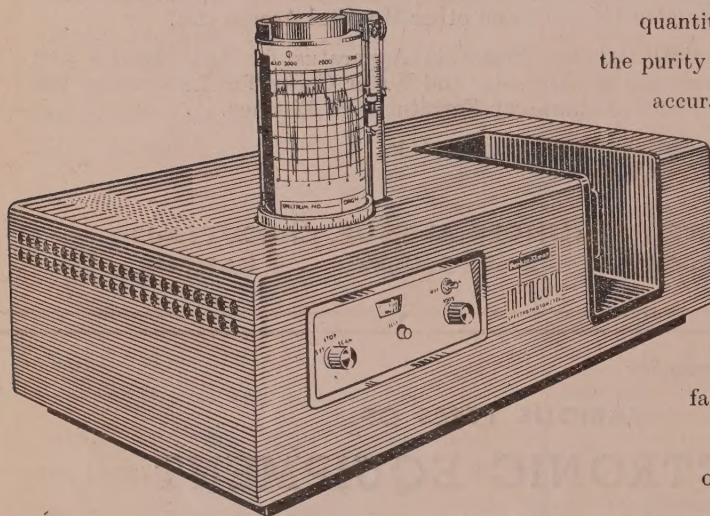
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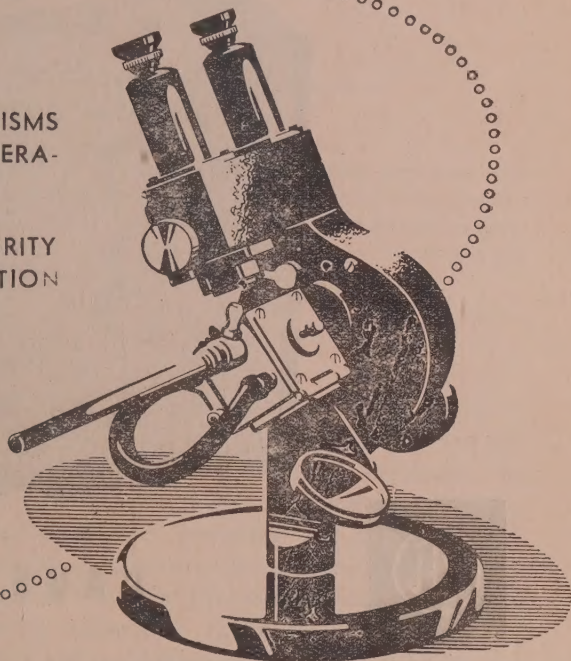
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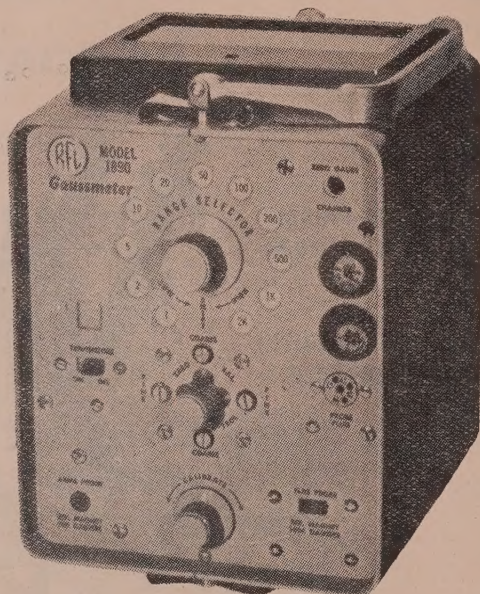
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ESTIMATION OF (Δr_e) OF AN ELECTRONIC BAND SYSTEM—A NEW METHOD

N. R. TAWDE AND A. P. WALVEKAR

DEPARTMENT OF PHYSICS, KARNATAK UNIVERSITY, DHARWAR

(Received June 28, 1960)

ABSTRACT A new method of constructing the Morse potentials associated with an electronic band system without the knowledge of internuclear distances and estimating therefrom the difference (Δr_e) in the equilibrium distances in the two states has been suggested. The knowledge of this latter quantity (Δr_e) is an essential parameter in the theories of vibrational transition probabilities in molecular spectra.

1

Morse potential becomes defined when equilibrium internuclear distances are known. But there are a number of band systems for which r_e values are not known, because of the difficulties of analysing the rotational structures. As such distances, or at least the difference between them for a transition, are essential for the problems of vibrational transition probabilities in electronic band spectra of diatomic molecules, it was thought worthwhile to explore the possibility of an indirect method, independent of rotational structure analysis to get a clue to the nearest, if not the precise estimate of the difference in internuclear equilibrium distances. The method and procedures are outlined in the following sections.

2

The usual Morse expression for potential energy

$$U = D_e(1 - e^{-a\xi})^2 \quad \dots (1)$$

can be converted to a slightly modified form

$$\frac{1}{a} \log_e \left(1 + \sqrt{\frac{u}{D_e}} \right) = (r - r_e) \quad \dots (2)$$

For $r_e = 0$, the Eq. (2) above becomes

$$\frac{1}{a} \log_e \left(1 + \sqrt{\frac{u}{D_e}} \right) = -r \quad \dots (3)$$

If a , u and D_e are assumed known, then the left hand side of Eqns. (2) or (3) above can be evaluated. These quantities are expressed as

$$a = 0.2454 \sqrt{\mu \omega_e x_e}$$

$$U(=E_v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2$$

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

Of these the quantity E_v is calculated for different values of v , i.e. 0, 1, 2, 3... and substituted in Eq. (2). We then get from it a set of values of $(r_e - r)$ corresponding to $E_0, E_1, E_2, E_3...$ etc, which we could designate as $r_0, r_1, r_2, r_3, ...$ etc. These are taken as one set of values about the equilibrium distance and are used for plotting the relevant part of the potential energy curve. It is then necessary to obtain points for other extremities of the vibrational levels for plotting the complementary part of the curve. This means another set of r values corresponding to E_0, E_1, E_2 and so on. For this purpose, since we are concerned with a harmonic oscillator the expression of Pillow (1951) can be made use of. According to Pillow, the centres of vibrational energy levels of an anharmonic oscillator lie at a distance of $(v+1)(x/a)$ from centres of the vibrational energy levels of the harmonic oscillator. Using this expression, the other set of r values will become

$$r_0 + 2(v_0 + 1) \frac{x}{a}$$

$$r_1 + 2(v_1 + 1) \frac{x}{a}$$

$$r_2 + 2(v_2 + 1) \frac{x}{a}$$

$$\dots \dots \dots \text{etc}$$

The method of arriving at the above type of expressions is indicated below.

The vertical axis is at a distance of r_0 (for $v = 0$ level) from the point of intersection of the potential energy curve and the vibrational energy level. As the centre of the vibrational energy level of the anharmonic oscillator lies at a distance $(v_0 + 1) \frac{x}{a}$ from the vertical axis, the centre of the vibrational energy level of the anharmonic oscillator is at the distance $r_0 + (v_0 + 1) \frac{x}{a}$ from the same point of intersection. So the distance from the vertical axis up to the point of intersection to the right will be

$$r_0 + (v_0 + 1) \frac{x}{a} + (v_0 + 1) \frac{x}{a}$$

or,

$$r_0 + 2(v_0 + 1) \frac{x}{a}$$

Now starting with $r_e = 0$, which may be taken as the origin and making use of these two sets of r -values and the vibrational energy E_v , the potential energy curves both for the upper and lower states of transition can be drawn. Some of these r -values for the $A^3\pi$ state of the C_2 molecule have been derived and shown in Table I.

TABLE I
Derived r -values for C_2 , $A^3\pi$ state.

v	$(v+1)x/a$ A.u.	$E_v(\text{cm}^{-1})$	$(-r)\text{\AA}$	$(+r)$ i.e. $r+2(v+1)(x/a)\text{\AA}$
0	0.003784	889.9	0.05206	0.05963
1	0.00757	2645.3	0.08596	0.10109
2	0.01135	4367.8	0.1074	0.1301
3	0.01514	6057.3	0.1241	0.15438
4	0.01862	7713.9	0.1374	0.17464
10	0.04162	16963.5	0.1902	0.27344

The assumption made above about the origin, i.e. $r = 0$ means that the two curves for the pair of the states involved are drawn about a common vertical axis. This is not enough as the curves need to be disposed with respect to the position of the minimum as well as with respect to their energy difference, i.e. the horizontal shift as well as the vertical shift. The steps for obtaining these relative dispositions are indicated below.

It is an established fact that if $\omega_e' > \omega_e''$ then $r_e' < r_e''$ and vice versa. So from the ω_e values, we know the direction in which the curve for the upper state is to be shifted with respect to the lower curve on the horizontal axis.

If the intensities of the bands are known fairly accurately or could be estimated, then it is possible to fix the Condon parabola or the most probable transitions. By trial the curve is shifted in the proper direction along horizontal axis until the most probable transitions known as above, are reached. When this is achieved carefully, one could get the nearest approximation to the quantity (Δr_e) .

To test the performance of the method outlined above, some well-established band systems were selected for study. Experimental intensity data as well as r_e -values in both the states are accurately known for these systems. One could construct the potential energy curves and derive the (Δr_e) value in the manner shown above. On the other hand, there is the knowledge of the exact value of this quantity from the rotational structure analysis constants. Both these values for the band systems chosen are recorded in Table II. How far the estimated values depart from exact experimental data is shown by calculating the percentage departure.

TABLE II
Comparative study

Molecule	Transition	Δr_e Å		Percentage departure from expl. value
		Present	Expl. value (Herzberg, 1950)	
C ₂ (Swan)	A $^3\pi - X^3\pi$	0.04	0.046	- 13.0
AlO	A $^2\Sigma - X^2\Sigma$	0.045	0.049	- 8.2
BO- α	A $^2\pi - X^2\Sigma$	0.160	0.1475	+ 8.8
BO- β	B $^2\Sigma - X^2\Sigma$	0.095	0.1061	- 10.4
CN-violet	B $^2\Sigma^+ - X^2\Sigma^+$	0.0225	0.0212	+ 6.1
N ₂ (IP)	C $^3\pi - B^3\pi$	0.055	0.0641	- 14.2
MgO	B $^1\Sigma - X^1\Sigma$	0.011	0.012	- 8.3

For certain band systems, estimates have been made by earlier workers on the basis of empirical relations or other methods. We can pick up one of these systems to see how far the forecast of (Δr_e) from the present method stands in relation to other estimates. The system to which we would refer is the (C-B) transition of BO. Katti (1957) by applying 4 different methods or rules has estimated the Δr_e -difference for this system. These estimates are recorded in Table III in which also, is included the value predicted from the present method.

TABLE III

Relation or method used	Δr_e -estimates	Å
Morse (1929)	0.1204	Katti (1957)
Birge (1932) and Mecke (1925)	0.1035	„
Wu and Chao (1947)	0.0720	„
Nicholls (1955)	0.1503	„
<i>Present method</i>	0.095	

It is evident from the results of Table III that the value derived from the method suggested here compares favourably with the data derived from other methods and particularly Birge and Mecke's relation. Although Katti is inclined to favour the value from Morse's relation, the approach made by the present method is the next best like Birge and Mecke's among the few methods or relations that are available. The true situation with regard to any of these methods will not be gauged unless we have in our possession the measured r_e -values from rotational structure analysis.

The advantage of the method is that it is entirely independent of any of the two r_e -values of the electronic states involved and requires the parameters, viz., ω_e and $\omega_e x_e$ which are generally provided by vibrational analysis and the knowledge of the most probable transitions from vibrational intensity data.

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RAMAN SPECTRA OF FLUOROBENZENE AT DIFFERENT LOW TEMPERATURES

DEB KUMAR MUKHERJEE

OPTICS DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION
OF SCIENCE, CALCUTTA 32

(Received, May 30, 1960)

Plate VII

ABSTRACT. The Raman spectra of fluorobenzene in the solid state at -60°C and at -180°C have been investigated and compared with the spectrum due to the liquid. At -60°C the crystals produce a new low-frequency line at 95 cm^{-1} and the line shifts to 100 cm^{-1} when the temperature is lowered to -180°C . This new line has been attributed to the formation of dimers at low temperature. Further, the Raman shifts of some prominent lines have been observed to change with solidification of the compound and lowering of temperature and these changes also have been attributed to the formation of dimers.

The polarisation of the Raman lines of the compound has been reinvestigated and it has been observed that the line 517 cm^{-1} is not totally depolarised and although the value of factor of depolarisation is quite large it is actually less than $6/7$.

INTRODUCTION

The Raman spectra of many mono- and disubstituted benzenes in the solid state at different low temperatures were studied by many previous workers. The Raman spectra of chlorobenzene and bromobenzene studied earlier by Ray (1950) and Biswas (1955) respectively showed that in the spectrum of frozen chlorobenzene at -60°C there are five new lines in the low frequency region the intensities and frequency-shifts of which increase when the temperature is lowered to -180°C . In the case of crystalline bromobenzene at -60°C only two new lines appear in the low frequency region while the number increases to three with lowering of temperature to -180°C . These results were interpreted on the hypothesis that the lines are due to small groups of molecules formed through virtual linkages in the solid state and the changes with temperature were attributed to the strengthening of these bonds and formation of fresh bonds at lower temperatures. The fluorobenzene molecule contains a highly active fluorine atom and the behaviour of this molecule in the solid state was not known. The Raman spectra of this compound at -60°C and at -180°C have, therefore, been investigated to find out the number of new low-frequency lines which may be produced by this compound in the solid state and the dependence of intensity and positions of the lines on temperature.

As regards the assignment of the Raman lines to different modes of vibration of the molecule as given in the Tables by Landolt-Börnstein (1951) the line 518 cm^{-1} has been assigned to a totally symmetric mode but the line has been described as a totally depolarised one. This is anomalous and therefore the polarisation of the Raman lines of this compound has been re-investigated to find out whether the discrepancy is genuine or not.

EXPERIMENTAL

Chemically pure sample of fluorobenzene obtained from Eastman Organic Chemicals Co. of New York was used in the present investigation and it was repeatedly distilled under reduced pressure before each exposure. The Raman spectra due to the substance in the liquid state and in the solid state at -60°C and at -180°C were photographed with the arrangements used by previous workers in this laboratory (Biswas, 1954). The intermediate temperature of -60°C was obtained by using as a refrigerant a mixture of alcohol and liquid oxygen in proper proportion in a Dewar vessel of Pyrex glass. All the Raman spectra were photographed on Ilford Zenith plates using a Fuess glass spectrograph giving a dispersion of about 11 \AA per mm. in the 4000 \AA region. Iron arc spectrum was also recorded on each spectrogram as comparison.

In order to study the polarisation of the Raman lines light from two horizontal mercury arcs was focussed with cylindrical condensers on the horizontal pyrex glass tube containing the liquid and the two components of the scattered light were focussed on the slit of the spectrograph one above the other with the help of a double image prism. With this arrangement the convergence of the incident light made the horizontal component of the totally depolarised line more intense than the vertical component. So, it was easy to find out the totally depolarised lines in the spectrum.

RESULTS AND DISCUSSION

Spectrograms showing the Raman lines due to fluorobenzene in the liquid state and in the solid state at different temperatures are reproduced in Figs. 1(a)—1(c) and the polarised Raman spectrum of the liquid is shown in Fig. 1(d). Plate V II. The low frequency line due to the solid at -60°C and -180°C is shown in the enlarged spectrograms in Figs. 2(a) and 2(b) respectively in the same plate.

The Raman frequencies due to the substance in the liquid and solid states are given in Table I. The Raman shifts due to the liquid reported by previous workers (Magat, 1936) are also given in the same table for comparison.

(a) *New Raman lines in the low frequency region*

It can be seen from Figures 2(a) and 2(b) and from Table I that only one broad new line at 95 cm^{-1} appears in the Raman spectrum due to the frozen fluorobenzene at -60°C , and the line becomes sharper and is shifted to 100 cm^{-1} when

TABLE I
Fluorobenzene, C_6H_5F
 $\Delta\nu$ in cm^{-1}

Liquid		Solid	
Magat, 1936	Present author at 30°C	at -60°C	at -180°C
		95 (7b) e, k	100 (7) e, k
243 (8) 6/7	242 (8b) \pm e, k ; D	255 (5) e, k	260 (2) e, k
424 (1)			
500 (0)			
518 (3) 6/7	517 (3) e, k ; P	510 (0) e, k	510 (1b) e, k
615 (2) 6/7	615 (2) e, k ; D	615 (0) e, k	615 (1b) e, k
705 (1)			
755 (1)	755 (1) e, k		
806 (9) 0,5	806 (6) e, k ; P	806 (5) e, k	806 (6) e, k
830 (1)			
883 (0) 6/7			
997 (2)	998 (1) e, k	996 (4) e, k	996 (5) e, k
1010 (10) 0,1	1009 (10) e, k ; P	1010 (4) e, k	1010 (4) e, k
1025 (1)			
1068 (1)	1068 (ob) e, k		
1157 (3) 6/7	1158 (4) e, k ; D	1158 (0) e, k	1158 (1) e, k
1220 (4) 0,5	1222 (3) e, k ; P	1214 (1) e, k	1214 (3) e, k
1280 (0)			
1413 (0)			
1498 (1)	1499 (2) e	1499 (0) e	1499 (1) e
1601 (4) 6/7	1602 (3b) e, k ; D	1603 (0b) e	1603 (1b) e
1625 (0)	1625 (0) e, k		
2615 (1)			
2917 (1)			
2986 (1)	2990 (0) k ?		
3027 (1)			
3074 (10) 0,1	3075 (12b) e, k ; P	3082 (5b)	3088 (7b) k
3090 (-)			
3180 (-)			
3677 (-)			

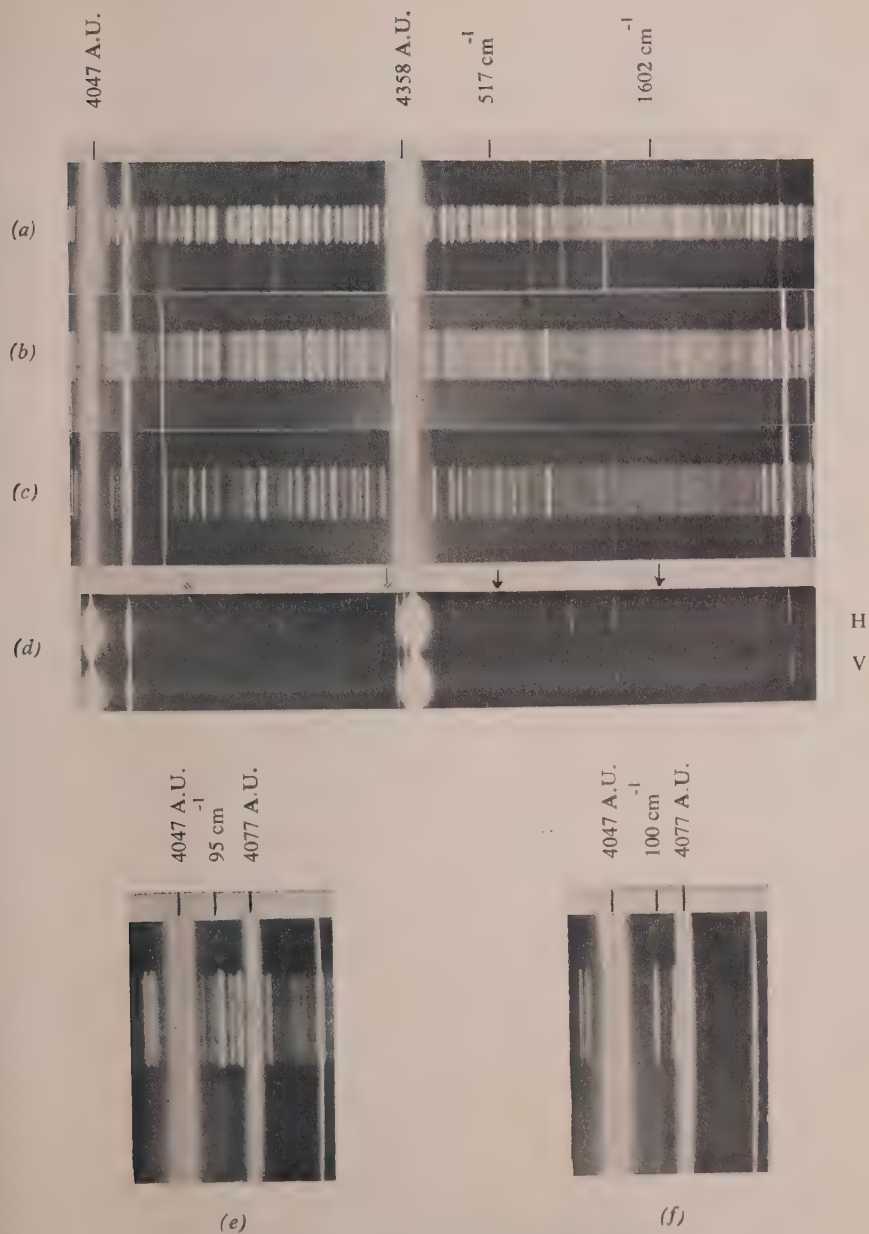


Fig. 1. Raman spectra of fluorobenzene.

- (a) Liquid at 30°C
- (b) Solid at -60°C
- (c) Solid at -180°C

- (d) Polarisation of Raman lines.
- (e) Showing low frequency Raman lines at -60°C
- (f) Showing low frequency Raman lines at -180°C

the temperature is further lowered to -180°C . The changes in the Raman shifts of the low frequency lines due to chlorobenzene and bromobenzene were reported previously by Ray (1950) and Biswas (1955) respectively. Ray (1950) observed five new lines in the case of chlorobenzene in the solid state both at -60°C and -180°C , while bromobenzene showed (Biswas, 1955) two such lines at -60°C and three new lines at -180°C . The crystal structures of the compounds were not known at that time but recently Biswas (1958) has reported that both the crystals of chlorobenzene and bromobenzene at -180°C belong to the same space group Q_h^{13} and also contain the same number of molecules per unit cell. If the new lines were due to lattice oscillations depending on the symmetry of the lattice the number of such lines would be the same in both these cases, but actually it is not so. The space group of fluorobenzene crystals is not known but the fact that other monosubstituted benzenes produce more than one line in the solid state while only one new line is observed in the case of fluorobenzene cannot be explained by the hypothesis put forward by Bhagavantam (1941) and Kastler and Rousset (1941) independently that angular oscillations of the molecules pivoted in the crystal lattice give rise to these new lines. Moreover, the amplitude of angular oscillation would decrease and consequently the intensity of the new line would diminish at lower temperatures, but actually the intensity of the line does not diminish with lowering of temperature from -60°C to -180°C .

Ray (1950) and Biswas (1955) concluded from the changes observed in the intensities and frequency-shifts of the low frequency lines in the case of crystals of chlorobenzene and bromobenzene respectively with lowering of temperature of the crystals that these lines might be due to oscillations in groups of molecules formed by virtual intermolecular linkages in the solid state as proposed by Sirkar (1936). Kastha (1958) recently found evidence of formation of such groups even in the liquid state just above the freezing point. The replacement of a bromine atom by the chlorine atom in the benzene ring may appreciably increase the affinity of the molecule to form intermolecular linkages with more distant neighbours increasing thereby the size of the associated groups and the number of the new Raman lines given by such groups. The situation is different in the case of fluorobenzene because fluorine being more reactive than chlorine the molecules may form dimers even in the liquid state just above the freezing point with a structure of the dimer in which the fluorine atom of each of the two molecules is attached to a hydrogen atom of the other molecule.

(b) *Shift of Raman lines of the molecule with solidification*

Table I shows that most of the Raman frequencies reported by Magat (1936) in the case of fluorobenzene in the liquid state have been observed in the present investigation. The line 242 cm^{-1} due to the liquid is found to shift to 255 cm^{-1} when the liquid is frozen and the temperature is lowered to -60°C and to 260 cm^{-1} at -180°C . The line 517 cm^{-1} shifts to 510 cm^{-1} when the liquid is frozen and

cooled to -180°C . The spectrum due to the liquid shows a feeble line with Raman shift 998 cm^{-1} and an intense line 1009 cm^{-1} . The line 998 cm^{-1} shifts to 996 cm^{-1} and becomes stronger with the solidification of the liquid and lowering of temperature to -60°C . This can be explained on the assumption that the line 996 cm^{-1} is due to dimers the number of which increases with solidification of the liquid. The line 1222 cm^{-1} observed in the liquid is shifted to 1214 cm^{-1} when the liquid is solidified. Further the Raman line 3075 cm^{-1} shifts to 3082 cm^{-1} with the solidification of the liquid and to 3088 cm^{-1} when the crystal is further cooled to -180°C .

On comparing the results with those due to bromobenzene (Biswas, 1955) it is found that the line 242 cm^{-1} of fluorobenzene behaves in the same way with solidification of the liquid and lowering of temperature as the line 182 cm^{-1} of bromobenzene. Biswas assigned the latter line to the vibration of type corresponding to the ϵ_u^{+} mode of the benzene ring given in Figure 1, No. 16 by Sponer and Kirby-Smith (1941) and the shift was attributed to the formation of virtual linkages between neighbouring molecules. In the present case also similar explanation holds good. The shift of the other lines mentioned above also lend support to the hypothesis that dimers are formed in the solid state of the substance.

(c) *Polarisation of the line 517 cm^{-1}*

The polarised Raman spectrum of liquid fluorobenzene shows that the horizontal component of the totally depolarised line 1602 cm^{-1} is more intense than the vertical component while the vertical component of the 517 cm^{-1} line is slightly more intense than the horizontal component. Hence the latter line is not totally depolarised and although the value of factor of depolarisation is quite large it is certainly less than $6/7$.

A C K N O W L E D G M E N T

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A TWO-DIRECTIONAL FOCUSING HIGH-INTENSITY MASS-SPECTROMETER

S. B. KARMOHAPATRO

SAHA INSTITUTE OF NUCLEAR PHYSICS, CALCUTTA

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ABSTRACT. A two-directional focusing high-intensity mass-spectrometer of focusing angle $\sqrt{2}\pi$ with mean radius 381 mm, variable 20 KV accelerating voltage, is described. Focusing properties and performance with a magnetic oscillation type ion source for gases are studied so that the instrument may be useful for studies of collision of ions in gases and solids, for preparation of isotopic targets and β -sources by direct deposition method.

INTRODUCTION

High-intensity mass-spectrometers or low-intensity electromagnetic isotope separators have recently become very important tools for research and many such instruments with ion currents ranging from 10^{-7}A to $100\text{ }\mu\text{A}$ have been constructed in different laboratories. Koch (1958) has reviewed these instruments, constructed so far and their application in laboratories for nuclear research. In the present paper we shall describe the constructional details of the development of a high-intensity mass-spectrometer consisting of a two-directional focussing magnetic analyser with a preliminary report of its performance.

THE MAGNETIC ANALYSER

The magnetic analyser, the main component of the mass-spectrometer, is designed after the β -ray spectrometer, originally constructed by Sieghban and Svartholm (1946) with some modifications. The choice of such two directional focussing $\sqrt{2}\pi$ magnet over other types for high-intensity mass spectrometry was dictated by the following considerations :

- 1) The axial focusing property of the analyser is of great advantage since it enables the direct deposition of β -ray sources or targets without any appreciable loss of the source materials used in the ion source.
- 2) The dispersion of such magnetic analysers is higher than that of the homogeneous magnetic analysers or the inhomogeneous ones as used by Zilverschoon (1954) and Artsimovich *et al.* (1957).
- 3) In spite of the disadvantages of the aberration factor which is higher for the two directional focussing magnetic analysers than the third order focussing, one, used by Zilverschoon (1954) the simplified conical shape of the pole faces

used by Arbman and Svartholm (1955) for a β -ray spectrometer or by Snyder *et al.* (1950) for a nuclear spectrometer could more easily be attained than shaping the inhomogeneity in the pole faces for third order focussing.

4) The accommodation of the ion source would have been convenient with a 180° -two directional focussing magnetic analyser described by Snyder *et al.* (1950). However with a $\sqrt{2}\pi$ focussing angle, the loss of ions is minimum and without any special device, space charge elimination can be accomplished with the electrons produced by the ion beam in collision with the residual gas as has been discussed by Zilverschoön (1954), since ions do not travel any distance out of the magnetic field.

The dimensions and the constructional details of the analyser with the focus-

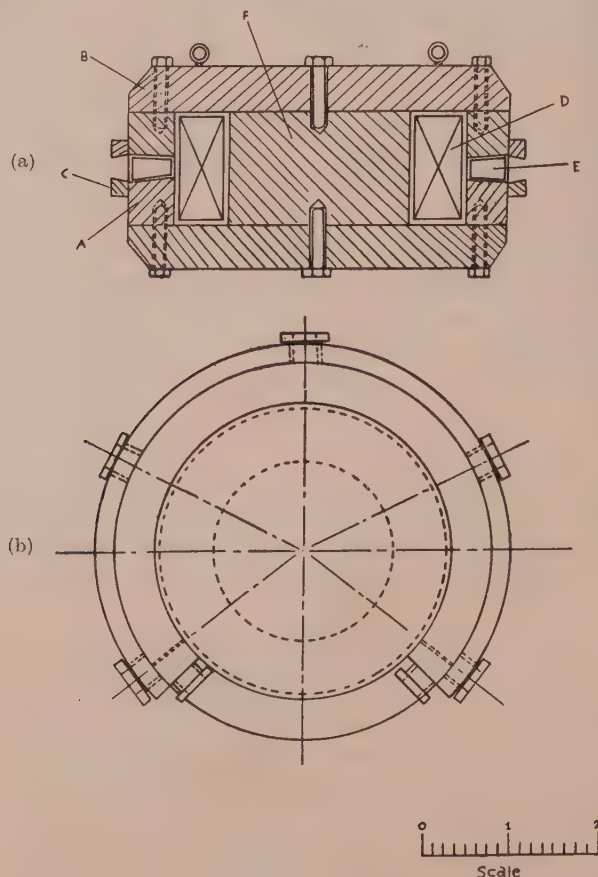


Fig. 1.—(a) Vertical section of the magnetic analyser with chamber: A and C—pole pieces with extension; B—yoke; D—coil; E—chamber.

(b) Horizontal section of the magnetic analyser with the vacuum chamber.

sing properties of the pole faces were previously described by the author (1959). The mean radius for the ions is kept at 381 mm at a gap width 5 cm as shown in Fig. 1(a) and 1(b). The vertical and horizontal sections of the magnetic analyser are shown in 1(a) and 1(b) respectively, along with the vacuum chamber.

In addition to the vacuum system described by the author (1959), a four-inch diffusion pump is now used on the ion source side for differential pumping of the residual gases and vapours. Both the diffusion pumps are operated with freon cooled baffles, so that the pressure of the chamber is maintained at $\sim 1 \times 10^{-5}$ mm Hg, when the ion source is operated with a gas. Liquid air traps are also provided to reduce the condensable vapours. The pressure is measured with thermocouple, penning and ionisation gauges.

THE ION SOURCE

A magnetic oscillation type ion source for gases is used with axial extraction as described by Nielsen (1957). The ion source (Fig. 2) consists of a ribbon filament (G), tips of which are water cooled, a cylindrical anode (H) of graphite with a 3/16 inch hole for the outlet of ions and outlet side is tapered at an angle of

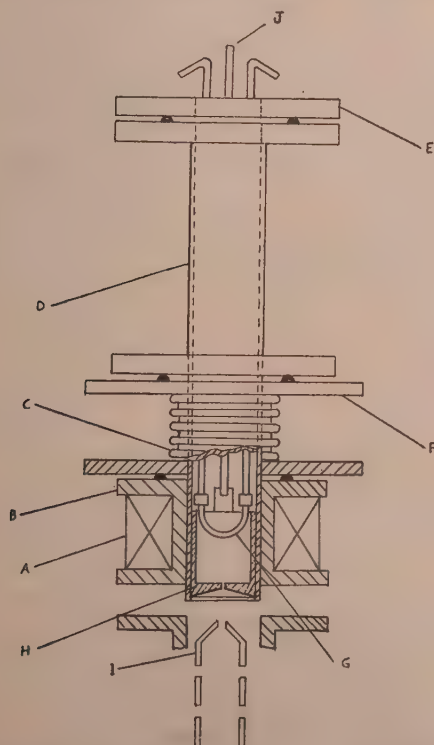


Fig. 2. Diagram of the ion source and the focussing electrodes.

55°. The whole system is on a brass flange (*E*) with electrical leads hermetically sealed. The tubular lead (*J*) connecting the anode serves as gas inlet adjustable through a needle valve. The source with flange is placed within a double-flanged specially made vitreosil tube (*D*) and made vacuum tight with rubber O-rings. One flange of the vitreosil tube is connected to the main vacuum chamber through a bellow (*C*) for slight adjustment of the system in space and a brass cylinder (*B*) containing the solenoid (*A*) for producing an axial magnetic field ~ 200 gauss for operating the ion source.

Three co-axial iron cylinders over the solenoid have to be used with spacers for screening the magnetic field of the main analyser, which might disturb the arc of the ion source. The ions are extracted through an electrode system consisting of three graphite cylinders, the first one (*I*) kept at a potential $\sim -1500V$, which can be varied for attaining the optimum condition. The second one is kept at a potential $0.75 V$, where V is the accelerating voltage and the third cylinder is at earth potential. Ions are electrostatically focused through this lens system and deflected by the magnetic analyser. The operating pressure in the source chamber is kept at $\sim 10^{-2}$ to 10^{-3} mm Hg approximately.

ELECTRONIC EQUIPMENTS

Resolving power of a mass- spectrometer greatly depends upon the stability of the magnetic field and the accelerating voltage. For attaining a specified resolution, the order of voltage stability required is only half of that of the magnetic field i.e. $\frac{\Delta H}{H} \sim \frac{\Delta V}{2V}$. So, it was decided to stabilise the magnetic field to 1/2000 and the accelerating voltage power supply to 1/1000. In stabilising the magnetic field, the current passing through the exciting coil is usually stabilised. For high impedance coils (D.C. 800 Ω resistance) of our magnetic analyser, a stabilised

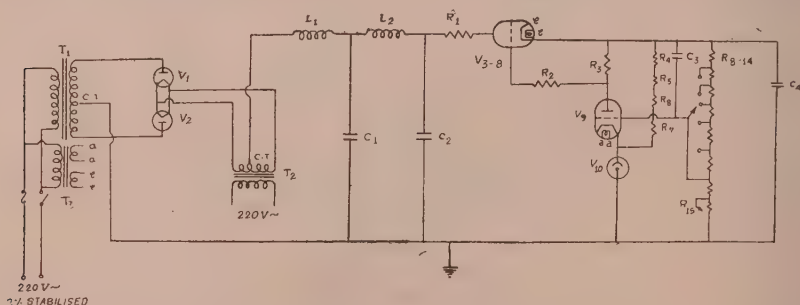


Fig. 3. Stabilised power supply for the magnet coils :

T_1 —Pri 220v, Sec 2000—0—2000v, 1.5A; T_2 —Pri 220v, Sec 2.5—0—2.5v, 30A; T_3 —Pri 220v, Sec 6.3v, 3A; 2.5v, 5A; L_1 , L_2 —20H, 1.5A ins. 2KV; C_1 , C_2 —16 μ fd, 2500v D.C; C_3 —1 μ fd, 2KV D.C; C_4 —4 μ fd, 1500V D.C; V_1 , V_2 —872A, V_3 —8—6336 (6); V_9 —2C53, V_{10} —5651; R_1 —100 Ω , R_2 —2K Ω , R_3 —4M Ω , R_4 —7—100K Ω , R_{3-14} —100K Ω , R_{15} —100K Ω Helipot (ten turns).

power supply was considered sufficient to attain short period stability of the magnetic field. Fig. 3 shows the circuit diagrams of the stabilised power supply +200 to +1500 V at 1.25A used for exciting the magnet coils. The use of 6336 (Chattham) series control tubes, high mu triode 2C53 as amplifier and 5651 as reference tube gives a stability of $\sim 1/2000$ to the magnetic field over the mains fluctuations stabilised to 0.2%, with an a.c. stabiliser (G.R). For a better stabilisation, a second feedback stage similar to that used by Pelchowich (1954) or to avoid long time instability a current stabilisation device will be required. For the present, neither of these improvements have been considered.

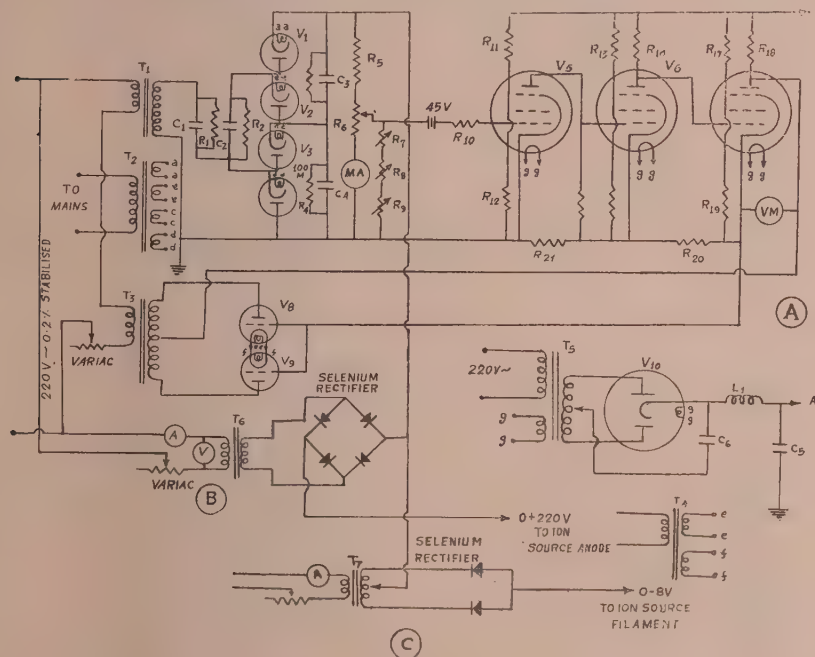


Fig. 4. Power supply for the ion source :

(A) Accelerating voltage 0-20KV (stabilised), (B) Arc voltage, (C) Filament heating supply, T_1 —Pri 220v, Sec 0-5KV, 50 mA (ins. 25KV), T_2 —Pri 220v, Sec 2.5-2.5, 10A (4) (ins. 25KV), T_3 —Pri 90v, Sec 400-0-400, 100mA, T_4 —Pri 220v, Sec 0-2.5v, 5A (2), T_5 —Pri 220v, Sec 350-0-350, 6.3v, 5A, T_6 —Pri 220v, Sec 0-8v, 100A, T_7 —Pri 220, Sec 0-220v, 2A, L_1 —5H, 100mA, C_1, C_2, C_3, C_4 —0.5 μ fd, 10 KV D.C., C_5, C_6 —2 μ fd, 500V, D.C., V_{1-4} —8020, V_{5-7} —6J7, V_{8-9} —2A3, V_{10} —6X5, R_{1-5} —100M Ω , R_6 —1K Ω , pot., $R_{7,8}$ —1M Ω , pot., R_9 —125 Ω , pot., $R_{10,11}$ —0.4M Ω , $R_{12,13}$ —0.1M Ω , R_{14} —0.4M Ω , R_{15} —0.1M Ω , R_{16} —30K Ω , R_{17} —10K Ω , R_{18} —100 K Ω , R_{19} —2.5K Ω , R_{20-21} —2K Ω ,

The 0 to +20 KV accelerating voltage power supply (Fig. 4) is a quadrupler rectifier from a 5 KV transformer, the primary of which is supplied with 0.2%

Fig. 5 shows the ion gauge circuit with devices for emission regulation, modified from a circuit used by Richard and Tuthill (1951).

For the safety of the ion gauge, its filament supply is interlocked with the heater supply of the diffusion pump by a circuit (Fig. 5) so that the ion gauge is protected when the heater supply breaks down. The backing mechanical pump is connected with the diffusion pump through a magnetic valve with air-admittance, which protects the diffusion pump oil from contamination with mechanical pump oil.

Fig. 6 shows a functional diagram of the mass-spectrometer with its different components.

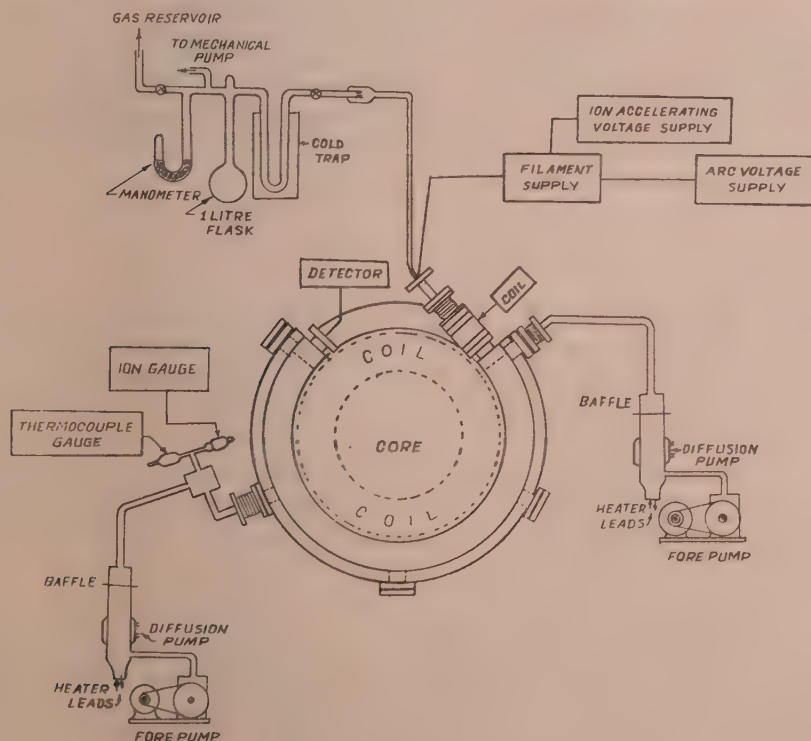


Fig. 6.—Functional diagram of the mass spectrometer.

PERFORMANCE

The performance of the mass spectrometer was tested by introducing neon and krypton gas in the ion source. Fig. 7 shows the photograph of the mass-spectrum of krypton from the oscilloscope screen, obtained by sweeping the ion-beam over a slit 1/32 inch wide by modulating the accelerating voltage with the

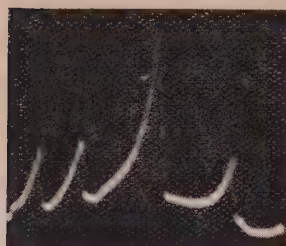


Fig. 7.—Oscillograph record of the mass spectrum of Krypton isotopes.
($M=82, 83, 84$ & 86).

following operating conditions : filament power ~ 230 Watts; arc voltage ~ 70 Volts; arc current ~ 400 mA ; accelerating voltage ~ 6 KV.

The oscillograph record shows some distortion due to the back-ground noise, when arc strikes and which can not be eliminated with the oscilloscope available. The current for the highest peak is estimated as $\sim 10^{-7}$ amp. The resolving power is measured to be ~ 125 , from the equation

$$R = \frac{x}{W_{\frac{1}{2}}} \cdot M$$

where x is the distance between two masses, $W_{\frac{1}{2}}$ is the half width, M is the mass number. The resolving power is found to be constant with the ions of neon and krypton for the accelerating voltage up to 8 KV, above which no reliable data at present were taken, because of the sparking between the ion source and negative electrode for extraction. Since the extraction of ions behaves as space charge limited current with this type of ion source, high accelerating voltage will enhance the focused ion beam. Moreover, the influence of the field of the main magnetic analyser over the focusing electrode, which are not fully shielded, may be somewhat responsible for the loss of the extracted current.

It is observed that the sparking is due to the rise in pressure on the ion source side and a diffusion pump of higher speed than the present one may improve the situation. Furthermore, better stabilisation of the accelerating voltage and the magnetic field, regulation of the arc, will be necessary to improve the resolving power of the instrument and the transmission may increase by modifying the ion source, extraction system and the vacuum system.

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THERMAL EXPANSION OF SOME ALKALI HALIDES BY X-RAY DIFFRACTION

P. D. PATHAK

DEPT. OF PHYSICS, GUJARAT UNIVERSITY, AHMEDABAD

N. V. PANDYA

M. G. SCIENCE INSTITUTE, AHMEDABAD

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ABSTRACT. In this paper the X-ray data on the thermal expansion of KBr, KI and CsBr upto their melting points is reported for the first time. The contribution of lattice defects to the thermal expansion is discussed. The applicability of the Debye-Grüneisen theory to explain the variation of thermal expansion with temperature is examined. An explanation of the difference in the observed values by the X-ray and the macroscopic methods is given, and an application of it to obtain a quantitative measure of the Schottky defects is indicated.

INTRODUCTION

In the field of solids, the study of the alkali halides has provided us with a number of most interesting properties. But when the literature about the variation of lattice constants with temperature by X-ray method is examined, we find that the crystals are not studied as a group. Scattered data are available on lattice constant variation (and hence on thermal expansion variation) with temperature, in some cases up to the melting point and in others within a limited range of temperature.

Reliable data on KBr and KI especially at high temperature are not available. Gott (1942) studied these salts between 20°C and 190°C but the X-ray expansion values obtained by him differ by about 5 per cent in the case of KBr and about 15 per cent in the case of KI from his values determined by the macroscopic methods, thus indicating a large concentration of defects (especially in KI). Connell and Martin (1951) repeated the observations under identical conditions and found their X-ray values agreeing closely with the macroscopic values of Gott.

The only X-ray data available so far up to the melting point of CsBr is that of Johnson, Agron and Breiding (1955). But their value of α at 25°C is about 20 per cent lower than that of Krishnan and Srinivasan (1956) obtained by precision interferometric method.

The present measurements were, therefore, undertaken (i) to provide accurate

X-ray data on the thermal expansion of KBr, KI and CsBr by employing a diffractometer, Geiger counter, ratemeter and an automatic chart recorder, (ii) to study the role of lattice defects on the thermal expansion and (iii) to examine the validity of the Debye-Grüneisen equations.

The diffractometer disc had a diameter of 500 mm. and was calibrated in degrees (2θ , each degree divided into four parts). The Geiger counter could be moved over the graduated scale either by means of a spherometer (whose disc had a diameter of about 70 mm.) or by a synchronous motor. The disc of the spherometer carried graduations so that readings of the counter positions could be read up to 1 minute of arc and by estimation up to $\frac{1}{2}$ minute.

OBSERVATIONS AND RESULTS

A special small furnace (Pathak and Pandya, 1959) which was fitted in the centre of the diffractometer was constructed in the laboratory. The temperatures were measured by a platinum-platinum plus 10% rhodium thermocouple. The furnace was calibrated by observing the meltings of (i) acetanilide (115°C), (ii) NaNO_3 (310°C), (iii) $\text{K}_2\text{Cr}_2\text{O}_7$ (400°C), (iv) CsCl (646°C), (v) KCl (790°C) and NaCl (800°C). The results on NaCl (Pathak and Pandya, 1959) and CsI (Pathak and Pandya, 1960) obtained by using the furnace have already been reported. Since the earlier results agreed with those of the most reliable workers, it was decided to extend the observations to other alkali halides. The results now obtained are given in Table I.

TABLE I

KBr		KI		CsBr	
Temperature degree C	Cell constant a_t Å	Temperature degree C	Cell constant a_t Å	Temperature degree C	Cell constant a_t Å
30	6.579	28	7.052	31	4.292
72	6.589	78	7.066	81	4.303
110	6.601	118	7.081	120	4.312
170	6.618	159	7.092	182	4.327
226	6.631	204	7.105	263	4.346
281	6.652	261	7.125	295	4.353
350	6.670	320	7.143	340	4.364
415	6.686	376	7.160	368	4.371
497	6.714	432	7.182	389	4.376
553	6.732	495	7.204	442	4.391
611	6.753	542	7.224	495	4.407
		601	7.244	540	4.422
				601	4.445

TABLE II

KBr		KI		CsBr	
Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$
30	38.6	28	40.4	31	47.8
72	39.4	78	41.6	81	50.0
110	40.0	118	42.5	120	51.6
170	41.1	159	43.4	182	54.1
226	42.2	204	44.5	263	57.3
281	43.1	261	45.7	295	58.6
350	44.3	320	47.1	340	60.4
415	45.5	376	48.4	368	61.4
497	46.9	432	49.6	389	62.3
553	48.0	495	50.9	442	64.4
611	48.9	542	51.9	495	66.4
		601	53.2	540	68.1
				601	70.3

TABLE III

$\alpha \times 10^6$					
Substance	Temperature range °C	Connell band		Gott (Macro- scopic) values)	Authors' (X-ray values)
		Martin (X-ray values)	Gott (X-ray values)		
KBr	18-100	40.5	38.8	40.8	39.2
	18-190	41.7	40.5	41.4	40.0
KI	20-100	40.6	37.2	40.8	41.2
	20-190	42.1	36.1	42.7	42.4

TABLE IV
Caesium bromide

Temperature degree C	$\alpha \times 10^6$		
	Authors' (X-ray values)	Krishnan & Srinivasan (Macroscopic values)	Johnson <i>et al.</i> (X-ray values)
0	46.6	46.6	37.2
31	47.8	48.0	39.5
81	50.0	50.3	43.0
120	51.6	51.9	45.7
182	54.1	54.5	50.0
263	57.3	57.6	55.5
295	58.6	58.7	57.7
340	60.4		60.8
368	61.4		62.7
389	62.3		64.1
442	64.4		67.6
495	66.4		71.0
540	68.1		74.0
601	70.3		77.8

The equations satisfying the smooth curves drawn from the observed points are given below :

$$\text{KBr} : -a_t = 6.5725 + 2.499 \times 10^{-4}t + 6.557 \times 10^{-8}t^2.$$

$$\text{KI} : -a_t = 7.0436 + 2.801 \times 10^{-4}t + 8.780 \times 10^{-8}t^2.$$

$$\text{CsBr} : -a_t = 4.2870 + 1.998 \times 10^{-4}t + 9.378 \times 10^{-8}t^2.$$

The coefficient of thermal expansion α was calculated from the equation

$$\alpha = \frac{1}{a_t} \cdot \frac{da_t}{dt}. \text{ The values of } \alpha \text{ thus obtained for the three salts are given in Table$$

II.

Our results are compared with those of the earlier workers in Table III and IV.

The satisfactory agreement between our values and those of Connell and Martin as well as with the macroscopic values of Gott at comparatively low temperatures indicates not too large a concentration of the migrated defects at the surface at these temperatures. (vide section 4)

It can be seen from Table IV that our results with CsBr agree quite satisfactorily with those of Krishnan and Srinivasan but disagree widely with those of Johnson *et al.*

DEBYE GRÜNEISEN EQUATIONS

Debye-Grüneisen theory gives (Roberts, 1951)

$$\frac{V_T - V_0}{K_0} \left\{ 1 - \frac{n+m+1}{2} \cdot \frac{V_T - V_0}{V_0} \right\} = \gamma E \quad \dots (1)$$

In this equation V_T and V_0 are the volumes of the crystal at $T^\circ K$ and $0^\circ K$ respectively, K_0 the compressibility at $0^\circ K$, E the vibrational energy of the crystal, γ the Grüneisen constant and m and n are constants obtained from the potential energy of the crystal,

$$W(V_0) = \frac{A}{V_0^n} + \frac{B}{V_0^m} \quad \dots (2)$$

The thermal expansion of a solid is always small so that $\frac{n+m+1}{2} \cdot \frac{V_T - V_0}{V_0}$

is small compared with unity. Neglecting it the Eq. (1) can be written as

$$V_T - V_0 = \gamma K_0 E \quad \dots (3)$$

Dividing both sides of the equation (1) by V_0 and transposing, we obtain

$$\frac{V_T - V_0}{V_0} = \frac{\gamma E K_0 / V_0}{\left\{ 1 - \frac{n+m+1}{2} \cdot \frac{V_T - V_0}{V_0} \right\}} \quad \dots (4)$$

Writing $Q = V_0 / \gamma \cdot K_0$ and $p = \frac{n+m+1}{2}$ in equation (4) we get

$$\frac{V_T - V_0}{V_0} = \frac{E/Q}{\left\{ 1 - p \cdot \frac{V_T - V_0}{V_0} \right\}} \quad \dots (5)$$

Substituting for $V_T - V_0$ in the small correction term from Eq. (3), Eq. (5) becomes

$$\frac{V_T - V_0}{V_0} = \frac{E/Q}{1 - p \cdot E/Q} \quad \dots (6)$$

Remembering that

$$\frac{V_T - V_0}{V_0} = 3 \cdot \frac{a_T - a_0}{a_0}$$

where a_T and a_0 are the lattice constants at $T^\circ K$ and $0^\circ K$ respectively, Eq. (6) can be written as

$$3 \cdot \frac{a_T - a_0}{a_0} = \frac{V_T - V_0}{V_0} = \frac{E/Q}{1 - p \cdot E/Q} \quad \dots (7)$$

In the case of alkali halides, E the vibrational energy is given by $E = 6RT \cdot D(\theta/T)$. Putting this value of E in Eq. (7) and transposing we get

$$\frac{a_0}{a_T - a_0} = \frac{Q}{2R} \cdot \frac{1}{T \cdot D(\theta/T)} - 3p \quad \dots (8)$$

This equation shows that the graph of $\frac{a_0}{a_T - a_0}$ against $\frac{1}{T \cdot D(\theta/T)}$ should be

a straight line. If for a given crystal the above graph is really a straight line, we can (i) show that the substance obeys Grüneisen's law and (ii) determine the Grüneisen's parameters $Q/2R$ and $3p$ from the graph.

The value of a_0 can be estimated from the low temperature approximation to Eq. (7)

$$\begin{aligned} 3 \cdot \frac{a_{273} - a_0}{a_0} &\approx \left(\frac{E}{Q} \right)_{273} \approx \left(\frac{3\alpha E}{C_v} \right)_{273} \\ &= \frac{3\alpha_{273} \cdot 273 \cdot D(\theta/273)}{C(\theta/273)} \end{aligned}$$

where $C(\theta/273)$ is the specific heat function and $\frac{C_v}{3\alpha} = Q = \text{constant}$ for low temperatures.

In the case of alkali halides investigated in the present experiments the graphs of $\frac{a_0}{a_T - a_0}$ against $\frac{1}{T \cdot D(\theta/T)}$ are straight lines, as predicted by the Grüneisen theory. The Grüneisen's parameters $Q/2R$ and $3p$, therefore, assume great importance. The parameters determined from the above graphs for the different halides are compiled in Table V. The values of these parameters for CsBr calculated from the X-ray measurements of Johnson *et al.*, are given for comparison.

TABLE V
Grüneisen parameters

Substance	$(Q/2R) \times 10^3$	$3p$	Reference
KBr	28.81	7.25	Present values
	28.60	—	Eq. 9
KI	27.12	6.50	Present values
	25.20	—	Eq. 9
CsBr	23.56	7.25	Present values
	27.10	10.80	Johnson <i>et al.</i> (1955)
	23.20	—	Eq. 9

The value of Q can also be obtained from the relation

$$Q = \frac{V_0}{\gamma \cdot K_0} \quad \dots \quad (9)$$

where K_0 and V_0 are the compressibility and molar volume at 0°K . The values of $Q/2R$ calculated from this equation are also given in Table V, the values of V_0 , γ and K_0 being taken from Born and Huang (1954).

ROLE OF LATTICE DEFECTS IN THE EXPANSION OF IONIC CRYSTALS

The fact that the ionic crystals conduct an electrolytic current which obeys Ohm's law at high temperatures shows that these crystals possess imperfections at elevated temperatures. It has been found that the ionic conductivity increases as the temperature increases showing that the concentration of the defects increases with temperature. Schottky (1935) and Jost (1933-37) have shown that it is exceedingly unlikely that interstitial ions occur in any appreciable quantity in alkali halides. Mott and Littleton (1938) have refined the calculations and have shown in the case of Sodium chloride, for example, that the energy required to take a Na^+ ion from a normal lattice position to an interstitial position is 2.9 eV, whereas the energy required to form a pair of vacancies is 1.86 eV. Thus the number of interstitial ions is very much less than the number of vacancies indicating that in alkali halides the Frankel defects are practically absent while the Schottky defects predominate.

As the temperature increases more and more ion pairs which were forming the part of the Schottky defects migrate to the surface. At the surface these ions are not surrounded by the bulk of the lattice and they cease to be defects. Now they could be reasonably expected to behave as fresh ions which are

deposited on the surface of an ionic crystal, forming the same structure as the bulk of the crystal. This happens because the ions are of the same type as constitute the crystal. These fresh deposits will increase the total volume of the crystal but will not modify the cell size. The cell size will alone be measured in the X-ray pictures, while in the macroscopic measurement of volume we measure the total volume (due to thermal expansion of the cell and that due to the surface deposits).

We are thus led to believe that the difference in the measured values of α by the X-ray and the macroscopic methods may be due to the fresh deposits at the surface due to the migration of the ions forming the Schottky defects. If this is correct we could expect the divergence in the two values to increase with the temperature. It thus appears plausible that we could estimate the degree and the extent of the migration of the defects by carrying out accurate measurements of α by the X-ray and the macroscopic methods. This work has been started by us and appears hopeful.

ACKNOWLEDGMENT

It is a pleasure to record our sincere thanks to Professor K. R. Dixit for useful discussion and help in preparing this paper.

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CHOICE OF SAMPLED WAVES FOR TIME-DIVISION MULTIPLEX TELEPHONE SYSTEMS

P. N. DAS

READER IN TELECOMMUNICATION ENGINEERING UNIVERSITY OF ROORKEE

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ABSTRACT. We can have multiplex telephone systems by using sampled voice signals on time division basis. These sampled voice signals may be used to operate the telephone receivers directly. The paper deals with the choice of the optimum frequency and width at which the voice signals are to be sampled in order that the telephone receivers may give the maximum output without having any appreciable distortion.

INTRODUCTION

Recently time-division principles have been applied to multiplex radio relay systems (Grieg and Levine, 1946) and pulse code modulation methods have been used in many of them (Black, 1947 and Fieldman 1948). The use of sampled waves in time-division working has some advantages in telephone systems and although their use in telephone systems has not yet been established, work is being carried on in this direction (Chattermole, 1958 and Price, 1958). Sampling frequencies of different values and of different width have been tried but no investigation appears to have been made with regard to the determination of the optimum values of the sampling frequency and its width. Sampled voice signals are just like pulse amplitude modulated signals but in them as the modulations are unidirectional, no demodulation is required and they can be used to operate the telephone receivers directly. An attempt has been made in this paper to determine the optimum values of the sampling frequency and its width when sampled voice signals are used to operate the telephone receivers directly.

TELEPHONE RECEIVER AND SAMPLED VOICE SIGNALS

In the case of sampled voice signals with square-topped pulses separated by spaces of no pulses, not only will the original voice signal be present but there will also be a very large number of beat frequencies formed by the frequencies of the original wave with the fundamental and odd harmonics of the sampling frequency. When the sampling frequency is greater than twice the highest frequency component present in the voice signal, all the frequency components of the voice signal will be present in the sampled wave according to Shanon's sampling theorem, but when a telephone receiver is subjected to such sampled voice signals, it will be subjected not only to the original voice signal but also to a very large

number of beat frequency components referred to above. It is, therefore, clear that if the telephone receiver is to give an exact reproduction of a voice signal from a sampled wave, the sampling frequency should not only be greater than double the highest frequency component present in the voice signal, but the sampling frequency should be such that none of the other wave packets associated with sampled wave may affect the telephone receiver.

When the number of channels to be worked on sampled voice signals on time-division basis is increased, the duration of the samples are to be necessarily decreased in proportion. Thus for a 100 channel system, the duration of the samples must at least be decreased to 1/100th part of the time between consecutive samples. When the duration of the samples is very small, however, compared to the time between consecutive samples, the telephone receiver may be assumed to be subjected to a series of impulses at the sampling points and the diaphragm may be assumed to be displaced to distances proportional to the total sum of the amplitudes of the impulses. In this case also the frequencies in the signal will be reproduced exactly when the sampling frequency is an exact multiple of them. This can be shown very easily mathematically. When they are not exact multiples, the sum total of the amplitudes due to the same frequency component will be different in different half cycles and sub-harmonics of the frequencies will be introduced. These have been illustrated in Figs. 1(a), 1(b), 1(c) and 1(d) for a few cases. As the voice signal consists of a band of frequencies, any one sampling frequency cannot be exact multiple of all the components. Therefore distortions are liable to be introduced. This distortion, however, decreases as the sampling frequency is increased and it is negligible when the sampling frequency is many times the highest frequency component present in the voice signal.

MATHEMATICAL TREATMENT

Suppose p is the angular frequency of the original wave and W is the angular frequency of the sampling rate.

Further, let $yW = xp$ where y and x are the two minimum possible integral numbers.

Then the angular distance between two consecutive samples will be given by

$$\theta = 2\pi \frac{y}{x}$$

If m samples correspond to n cycles of the wave.

Then $\theta.m. = n.2\pi$ (m and n are integral numbers)

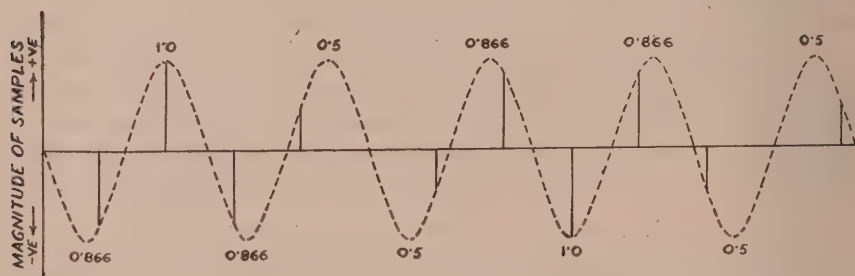
or
$$n = \frac{\theta.m.}{2\pi} = \frac{2\pi y}{x} \frac{m}{2\pi} = \frac{y}{x} \cdot m$$

Thus for given values of y/x , m will be of such value that n becomes an integer.

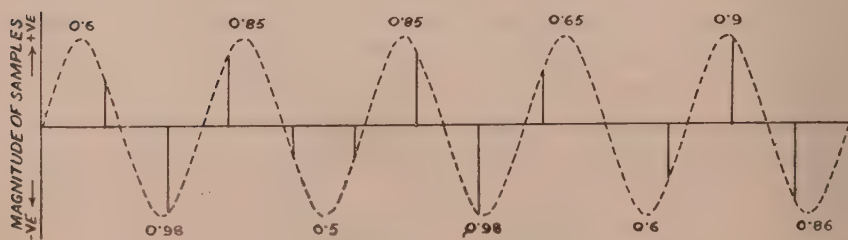
When $W = 2p, 3p, 4p$ etc, n will become equal to 1. Therefore in each cycle there will be a definite number of samples and it can be shown that the total magnitude of the samples in each half portion is also equal. Therefore if a telephone receiver be subjected to such sampled waves instead of the continuous wave, it will give the same reproduction.

When, however, y/x has a value such that y has got a value other than 1, n will also have a value other than 1. In such a case a fixed number of samples cannot be contained in each cycle of the wave and so the samples in each cycle will be differently distributed but a definite number of samples will be repeated after every few and definite number of cycles of the wave, this number of cycles being given by the value of n . Further, the sum total magnitude of the samples in each half cycle will not be of the same value and a sub harmonic of the order of the value n will be introduced.

If a band of frequencies, say, voice frequencies are, therefore, sampled and a receiver is subjected to such a sampled wave, a few frequency components whose direct multiples will be the sampling frequency, will be correctly reproduced and others will be distorted. It is to be noted, however, that higher the values of sampling rates, greater will be the number of samples present in each half cycle of each component and less will be the differences in total magnitude of the samples. These will be evident from Figs. 1(a), 1(b) 1(c) and 1(d). Therefore, for good

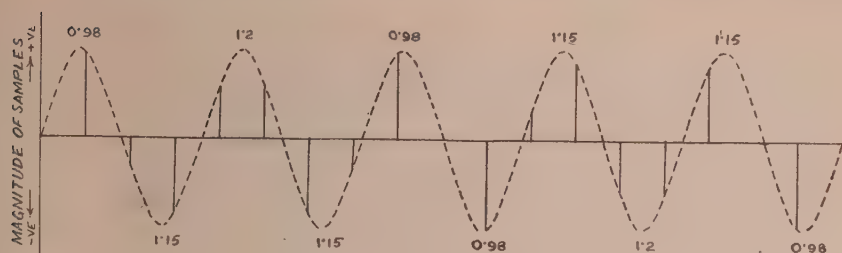


(a) $\theta = 150^\circ$; $p = \frac{5}{12}\omega$; $\omega = 2\frac{2}{3}p$.

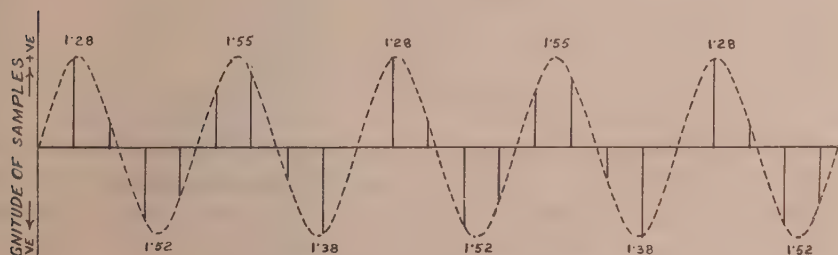


(b) $\theta = 140^\circ$; $p = \frac{7}{6}\omega$; $\omega = 2\frac{4}{7}p$.

Fig. 1(a) & 1(b). Total magnitude of pulses in different half cycles when sampling is done at a frequency which is not an exact multiple of the frequency of the wave.



$$(c) \theta = 100^\circ, p = \frac{5}{18}\omega, \omega = 3\frac{3}{5}p$$



$$(d) \theta = 90^\circ, p = \frac{2}{9}\omega; \omega = 4\frac{1}{2}p$$

Fig. 2(c) & (d). Total magnitude of pulses in different half cycles when sampling is done at a frequency which is not an exact multiple of the frequency of the wave.

reproduction purposes, the sampling frequency should be quite a number of times the highest frequency component present in the voice signal. As discussed afterwards, it has been experimentally found that the sampling frequency should be at least 4 times the highest frequency component present in the voice signal, in order that the distortions in the output of the telephone receiver may be negligible.

METHODS OF PRODUCING SUITABLE SAMPLED WAVES

Germanium diodes in the form of a bridge have been used by the author elsewhere (Das, 1957) in producing sampled waves as shown in Fig. 2. The bridge shows a low resistance between the points *A* and *B* when *C* is at a higher potential than *D* and it shows a very high resistance when *C* is at a lower potential than *D*. If an alternating voltage referred to as the switching voltage be applied between *C* and *D*, then the bridge will be made conducting and non-conducting alternately between the points *A* and *B* and the bridge will behave like a switch between *A* and *B*. If pulses are used as switching voltage in series with a bias voltage as shown, then also the bridge will be conducting during pulse periods only if the pulse voltage is greater than the bias voltage. Pulses of varying frequency and varying width are obtained by triggering a monostable multivibrator

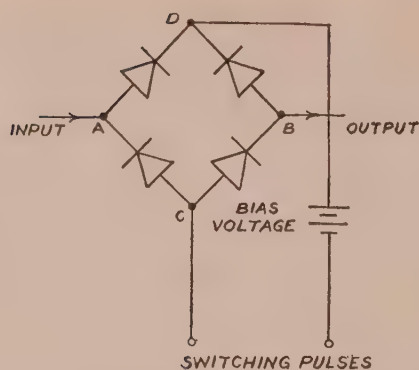


Fig. 2. Bride switching circuit with Bias voltage.

with a blocking oscillator. The frequency of pulses is changed by changing the frequency of triggering pulses with the help of the blocking oscillator and the duration of the pulses is changed with the help of the monostable multivibrator used. Thus using such pulses as switching voltages, we can get the sampled waves of different sampling frequency and of different width.

EXPERIMENTAL

(i) Optimum sampling frequency

The experimental arrangement is shown in Fig. 3. The switching voltage obtained in the way described above is applied to the bridge circuit consisting of four germinium diodes in series with a bias battery voltage of 5 volts. The audio signal was obtained from an audio oscillator and the sampled

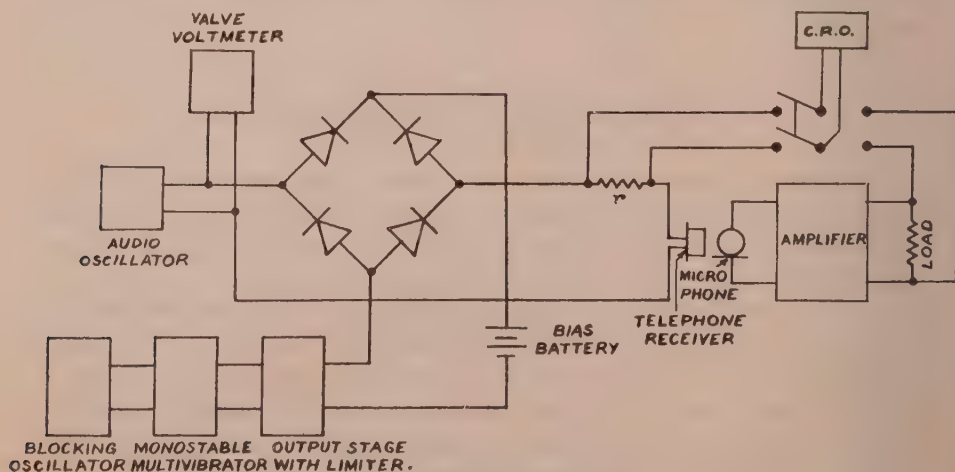


Fig. 3. Experimental arrangement.

wave obtained was connected directly to a telephone receiver. The output of the telephone receiver is fed to a microphone and the output signal from the microphone is amplified by means of an amplifier whose output was studied with a C.R.O. When the sampling frequency was above 10 Kc/s, the output of the telephone receiver was found to be an exact reproduction of the audio signal over the entire voice signal range up to 3 Kc/s irrespective of the width of the samples. When the sampling frequency was lower than 10Kc/s, but an exact multiple of the audio signal, then also the output was found to be an exact reproduction of the signal which was sampled. When, however, the sampling frequency was less than 10Kc/s and not an exact multiple of the audio signal frequency, distortions were found to be present in the output and these distortions varied as the sampling frequency was changed evidently due to the different sub-harmonics that were present in the different cases. One such distorted signal as seen in C.R.O. for a sinusoidal wave is shown in Fig. 4(a). When, however, the sampling frequency was 10 Kc/s and above, the output of the same audio wave as seen in C.R.O. is as shown in Fig. 4(b).

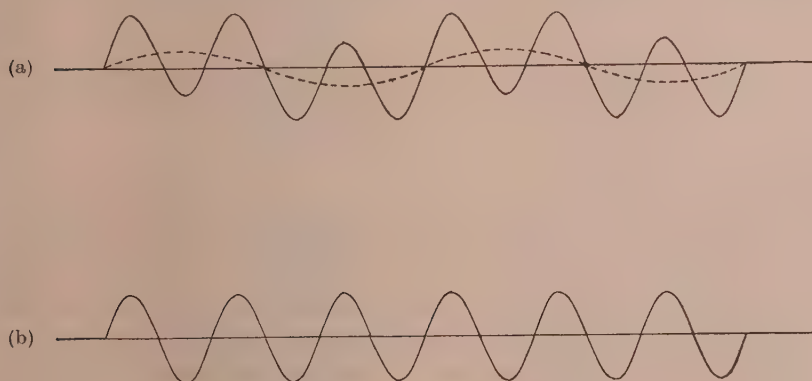


Fig. 4. (a) Output of a sinusoidal signal when sampling frequency is not an exact multiple of the signal and much below 10 Kc/s.

(b). Output of the same sinusoidal signal when the sampling frequency is 10 Kc/s.

(ii) *Optimum width of samples*

The power of the original wave is theoretically proportional to t^2/T^2 in the sampled wave where t is the width of the sample and T is the time interval between consecutive samples. Therefore, if keeping the sampling frequency constant, its width is decreased, the power of the original wave in the sampled wave will also be decreased and in order to get the same power output the power of the original wave has to be increased before it is sampled. This has been experimentally determined with the same experimental arrangement, with the slight modification by which the output can be measured. The results obtained are

shown in Fig. 5. Excess power in *db* required in audio signals of 1000 c.p.s. before it is sampled in order that the sampled waves may give the same audio signal output in a telephone receiver, has been plotted against width of samples of different sampling frequency. It is seen that smaller the width of the samples, larger the power required in the audio signals for giving the same output from

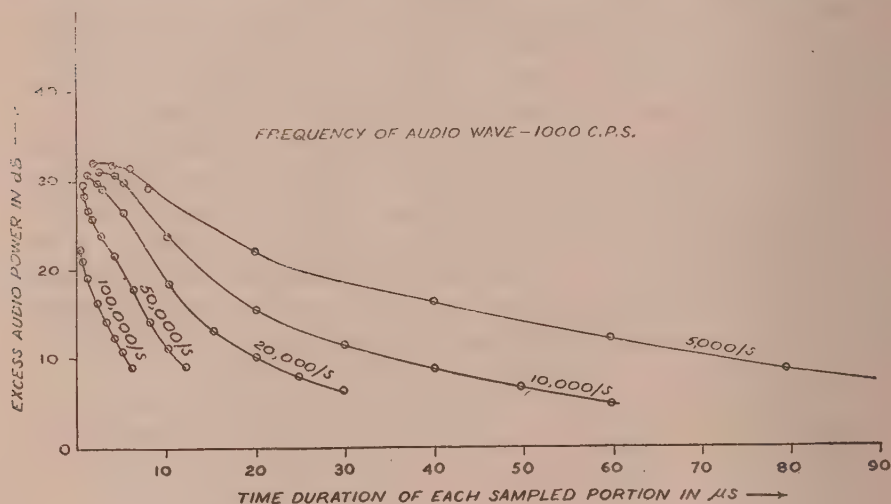


Fig. 5.

the sampled waves. The maximum width of samples is, however, determined by the sampling frequency and the number of channels in the system. With 10 Kc/s as the sampling frequency, the value of T is fixed i.e. 100 μ -secs. Thus for a 10-channel system, the maximum theoretical value of the width of the sample can be 10 μ -secs. If we are to give a margin of 100 p.c. distortion, the width of the samples will be limited to 5 μ -secs only. With such samples the audio signal has to be increased in power by about 30 db before sampling if the telephone receiver is to give the same output as the original audio signal.

DISCUSSION

When a telephone receiver is directly operated by sampled voice signals, the sampling frequency having a value equal to double the highest frequency component present in voice signals, the reproduction is not satisfactory because of the beat frequency components formed by the fundamental and odd harmonics of sampling frequency. For instance, if the sampling frequency is three times a particular frequency component in the voice signal, then the second harmonic will be introduced by the lower beat. For this reason although 3 Kc/s may be taken as the highest frequency component of the voice signals, a sampling frequency of 6 Kc/s does not reproduce the original signal faithfully. The beat frequencies

formed by higher harmonics present in the square-topped signals may be negligible but the beat frequency formed by the fundamental of the sampling frequency cannot be neglected. An ordinary telephone receiver is not very sensitive above 7 Kc/s. Hence if the beat frequency formed by any component of the voice signal with at least the fundamental of the sampling frequency does not come within 7 Kc/s, the reproduction is not distorted. As the highest frequency component present in voice signals may be taken as 3 Kc/s, the lowest sampling frequency necessary is 10 Kc/s as experimentally determined.

When the samples are of very short durations, distortion due to the sampling frequency being not an exact multiple of any voice signal frequency, is also negligible when the sampling frequency is at least 10 Kc/s. The maximum width of the samples that can be used is limited by the number of channels for a particular sampling frequency. It is to be noted, however, that when the number of channels is increased and the width is necessarily decreased it is not necessary to increase the power of the audio signal proportionately as shown by the flat nature of curves of Fig. 6 towards the smaller width regions. As it is desirable to use the lowest value of sampling frequency, 10 Kc/s is the optimum value for sampling voice signals to be used for working telephone receivers and the optimum width of the samples is determined by the number of channels in the system.

ACKNOWLEDGMENT

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Letters to the Editor

The Board of Editors will not hold itself responsible for opinions expressed in the letters published in this section. The notes containing reports of new work communicated for this section should not contain many figures and should not exceed 500 words in length. The contributions must reach the Assistant Editor not later than the 15th of the second month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors.

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FORCE CONSTANTS OF THE URANYL ION BY WILSON'S F-G MATRIX METHOD

K. V. NARASIMHAM

(APPLIED PHYSICS DEPARTMENT, MADRAS INSTITUTE OF TECHNOLOGY, CHROMEPET, MADRAS)

(Received, April 2, 1960)

The force constants of the UO_2^{++} ion in caesium uranyl nitrate have been calculated by the Wilson's normal coordinate treatment (1939 and 1941) for both the bent and linear structures (C_{2v} and $D_{\infty h}$ point groups respectively). The vibrational frequencies, bond length and bond angle are taken from the data reported by Dieke and Duncan (1949). They are as follows :

Symmetric stretching frequency	883.98 cm^{-1}
Symmetric bending frequency	213.16 ,,
Antisymmetric stretching frequency	956.20 ,,
Bond length 1.58 Å.	Bond angle 135°.

For the bent uranyl ion, four constants F_d , F_{dd} , F_d and F_d are to be calculated and there are only three frequencies for the ion. Therefore, the value of F_d calculated by Satyanarayana (1942) using the equations given by the valence force field theory has been taken. The value is 6.97×10^5 dynes/cm. Assuming this value of F_d , the other potential constants are calculated by the F-G matrix method.

For the linear uranyl ion, the G matrix elements are obtained from the tables of Decius (1948). But a deficiency occurs in his tables when a molecule contains three or more collinear nuclei as in the expressions for the **s**-vectors given by Wilson for bending coordinates, the denominator becomes zero. Therefore, Ferigle and Meister (1951) have given alternate expressions for the kinetic energy

matrix elements of the bending co-ordinates for linear molecules, from which the g matrices of the bending coordinates of the UO_2 ion are calculated.

TABLE

Force constant	Description	Bent UO_2 ion (C_{2v}) ($\times 10^5$ dynes/cm.)	Linear UO_2 ion ($D_{\infty h}$) ($\times 10^5$ dynes/cm.)
f_d	O-U stretching	+6.97	+7.49
f_{dd}	Interaction between the two bonds	-0.77	-0.12
f_α	O-U-O bending	+0.47	+0.20
$f_{d\alpha}$	Interaction between the bond and angle	-2.81	0

The author is thankful to Dr. V. Santhamma for her help in the course of the calculations and to Dr. V. Ramakrishna Rao for his interest in the work.

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14

PHASE-TRANSITIONS IN $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$

(Miss) GOURI BHOWMIK

DEPARTMENT OF MAGNETISM, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
 JADAVPUR, CALCUTTA-32.

(Received, August 8, 1960)

Magnetic measurements showed (Bose, *et al.*, 1957 & 58) that the single crystals of many Tutton salts (composition : $\text{M}(\text{AXY})_2 \cdot 6\text{H}_2\text{O}$) lost their magnetic anisotropies in the range 65° — 120°C , probably due to a phase transition taking place which caused the single crystal to become polycrystalline. As a preliminary to studying the change in magnetic properties of the substance with change in structures, a study of the thermal dehydration of a typical case—that of $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$, was undertaken which shows that there is a loss of 4 molecules of water at 67°C . The crystal structure of the dehydrated product was then

studied from X-ray powder photograph. It is found that the dehydrated product consists of the double salt $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 2_2\text{H}_2\text{O}$. Application of Lipson's method (Lipson, 1949) shows that it has an orthorhombic unit cell having dimensions: $a = 14.84\text{\AA}$, $b = 12.52\text{\AA}$, $c = 10.69\text{\AA}$ containing 8 molecules per cell. Conditions of reflection suggest the possibility of assigning to the dihydrate either of the space-group $P_{mn} 2_1$ or P_{mmm} .

Since direct X-ray data on $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ single crystal is lacking, we also undertook to study it and find that the hexahydrate which belongs to the space-group $P2_1/a$ and contains 2 molecules in the unit cell (Hofmann, 1931), has the following cell dimensions: $a = 9.27\text{\AA}$, $b = 12.50\text{\AA}$, $c = 6.33\text{\AA}$, $\beta = 106.5^\circ$.

It is interesting to note that the b axis in both the hexa- and dihydrate has the same length. It is, therefore, probable that the transition from the monoclinic to the orthorhombic system has taken place after merely a loss of 4 water molecules and a rearrangement of the molecules with reference to two vertical planes i.e., the transition is "topotactic" in nature.

Phase transition study for further dehydration and a more detailed study of structural changes by growing single crystals at high temperatures are under progress.

The author expresses her sincere thanks to Prof. A. Bose, D.Sc., F.N.I., for his kind interest and constant guidance and to Mr. S. Ray, M.Sc., for many helpful discussions during the progress of the work.

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15

F-G MATRIX ELEMENTS FOR PYRAMIDAL XY_2Z MOLECULES

P. BABU RAO AND K. SREERAMAMURTY

PHYSICS DEPARTMENT, S. V. UNIVERSITY COLLEGE, TIRUPATI

(Received July 7, 1960)

Using Wilson's F-G matrix methods (1939, 1941), Pistorius (1959) obtained the elements for the planar XY_2Z type molecules employing the most general harmonic force field. These were recalculated by the authors (1960) and utilised to calculate the potential constants for certain specific cases. Venkateswarlu and Sundaram (1957) carried out a normal coordinate treatment for the pyramidal

XY_2Z type molecules neglecting a number of force constants. As a large number of these molecules are known and as their structural constants are being found by microwave techniques, it is felt desirable to carry out a similar calculation for this type of molecules employing the most general harmonic force field.

The following symmetry coordinates are set up which transform according to the characters of the corresponding vibration types.

$$A' : R_1 = \frac{1}{\sqrt{3}}(\Delta D + \Delta d_1 + \Delta d_2)$$

$$R_2 = \frac{1}{\sqrt{6}}(2\Delta D - \Delta d_1 - \Delta d_2)$$

$$R_3 = \frac{d}{\sqrt{3}}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\beta)$$

$$R_4 = \frac{d}{\sqrt{6}}(2\Delta\beta - \Delta\alpha_1 - \Delta\alpha_2)$$

$$A'' : R_5 = \frac{1}{\sqrt{2}}(\Delta d_1 - \Delta d_2)$$

$$R_6 = \frac{d}{\sqrt{2}}(\Delta\alpha_1 - \Delta\alpha_2)$$

Here ΔD and Δd represent the $X-Z$ and $X-Y$ stretchings, $\Delta\alpha$ and $\Delta\beta$ the valence angle bendings of $Y-X-Z$ and $Y-X-Y$ respectively.

The potential energy V is given by

$$\begin{aligned} 2V = & f_D \cdot \Delta D^2 + f_d \sum_i \Delta d_i^2 + 2f_{Dd} \cdot \Delta D \sum_i \Delta d_i \\ & + 2f'_{dd} \Delta d_1 \Delta d_2 + 2f_{Da} \Delta D \cdot d \sum_i \Delta\alpha_i + 2f_{da} \cdot d \cdot \sum_i \Delta d_i \Delta\alpha_i \\ & + 2f'_{aa} \cdot d \sum_i \Delta d_i \Delta\alpha_j + 2f_{d\beta} d \sum_i \Delta\beta \Delta d_i \\ & + 2f_{D\beta} \Delta D \cdot d \Delta\beta + f_a d^2 \sum_i \Delta\alpha_i^2 + 2f_{aa} d^2 \Delta\alpha_1 \Delta\alpha_2 \\ & + 2f_{a\beta} d^2 \Delta\beta \sum_i \Delta\alpha_i + f_\beta d^2 \Delta\beta^2 \end{aligned}$$

The following F matrix elements are obtained :

$$A' : F_{11} = \frac{1}{3} (f_D + 4f_{Dd} + 2f_1)$$

$$F_{12} = \frac{1}{3\sqrt{2}} (2f_D + 2f_{Dd} - 2f_1)$$

$$F_{13} = \frac{1}{3} (2f_{D\alpha} + f_{D\beta} + 2f_2 + 2f_{d\beta})$$

$$F_{14} = \frac{1}{3\sqrt{2}} (2f_{D\beta} + 4f_{d\beta} - 2f_{D\alpha} - 2f_2)$$

$$F_{22} = \frac{1}{6} (4f_D - 8f_{D\alpha} + 2f_1)$$

$$F_{23} = \frac{1}{3\sqrt{2}} (4f_{D\alpha} + 2f_{D\beta} - 2f_2 - 2f_{d\beta})$$

$$F_{24} = \frac{1}{6} (4f_{D\beta} - 4f_{D\alpha} + 2f_2 - 4f_{d\beta})$$

$$F_{33} = \frac{1}{3} (2f_3 + 4f_{\alpha\beta} + f_\beta)$$

$$F_{34} = \frac{1}{3\sqrt{2}} (2f_{\alpha\beta} + 2f_\beta - 2f_3)$$

$$F_{44} = \frac{1}{6} (4f_\beta + 2f_3 - 8f_{\alpha\beta})$$

Where f_1, f_2 and f_3 stand for

$(f_d + f_{dd}), (f_{d\alpha} + f'_{d\alpha})$ and $(f_\alpha + f_{\alpha\alpha})$ respectively.

$$A' : \quad \begin{aligned} F_{55} &= f_d - f_{dd} \\ F_{56} &= f_{d\alpha} - f'_{d\alpha} \\ F_{66} &= f_\alpha - f_{\alpha\alpha} \end{aligned}$$

The elements of the inverse kinetic energy (G) matrix are given below using the following abbreviations :

$$\begin{aligned} d/D - \cos \alpha &= K & 1 + \cos \alpha + \cos \beta &= Q \\ 1 - d/D \cos \alpha &= L & 1 + \cos \beta - 2 \cos \alpha &= T \\ 1 - \cos \alpha &= M_\alpha & 1 + \cos \beta - 2 \cos^2 \alpha &= V \\ 1 - \cos \beta &= M_\beta & \cos \alpha = c_\alpha, \quad \sin \alpha &= S_\alpha \\ 1 + \cos \beta &= N & & \\ 1 + 2 \cos \alpha &= P & \cos \beta = C_\beta, \quad \sin \beta &= S_\beta \end{aligned}$$

μ_i = Reciprocal mass of the atom i

$A' :$

$$G_{11} = \frac{1}{3} \left[\mu_x \{2(N+P)-1\} + 2\mu_y + \mu_z \right]$$

$$G_{12} = \frac{\sqrt{2}}{3} \left[\mu_x (P-Q) - \mu_y + \mu_z \right]$$

$$G_{13} = -\frac{2}{3} \mu_x \left[\frac{KQ+LP}{S_\alpha} + \frac{2M_\beta Q}{S_\beta} \right]$$

$$G_{14} = -\frac{\sqrt{2}}{3} \mu_x \left[\frac{KQ+LP}{S_\alpha} + 2 \frac{S_\beta^2 + C_\alpha M_\beta}{S_\beta} \right]$$

$$G_{22} = \frac{1}{3} [\mu_x(2T+M_\beta) + \mu_y + 2\mu_z]$$

$$G_{23} = \frac{\sqrt{2}}{3} \mu_x \left[\frac{KT-2LM_\alpha}{S_\alpha} + \frac{M_\beta T}{S_\beta} \right]$$

$$G_{24} = \frac{1}{3} \mu_x \left[\frac{KT-2LM_\alpha}{S_\alpha} + \frac{2M_\beta T}{S_\beta} \right]$$

$$G_{33} = \frac{2}{3} \left[\mu_x \left\{ \frac{K^2N+2L^2+4C_\alpha KL}{S_\alpha^2} + M_\beta + \frac{2M_\beta NK+8C_\alpha M_\beta L}{S_\alpha S_\beta} \right\} \right. \\ \left. + 2\mu_y \left(1 + \frac{C_\alpha M_\beta}{S_\alpha S_\beta} \right) + \mu_z \frac{d^2}{D^2} \frac{V}{S_\alpha^2} \right]$$

$$G_{34} = \frac{\sqrt{2}}{3} \left[\mu_x \left\{ 2M_\beta + \frac{S_\beta^2 K + 2C_\alpha ML}{S_\alpha S_\beta} - \frac{NL^2 + 2L^2 + 4C_\alpha KL}{S_\alpha^2} \right. \right. \\ \left. \left. + \mu_y - \mu_z \frac{d^2}{D^2} V \right\} \right]$$

$$G_{44} = \frac{1}{3} \left[\mu_x \left\{ 4M_\beta + \frac{M_\beta K^2 + 2L^2 + 4C_\alpha KL}{S_\alpha^2} - 4 \frac{S_\beta^2 K + 2C_\alpha ML}{S_\alpha S_\beta} \right\} \right. \\ \left. + \mu_y \left(5 - \frac{4C_\alpha M_\beta}{S_\alpha S_\beta} \right) + \mu_z \frac{d^2}{D^2} \frac{V}{S_\alpha^2} \right]$$

$A'' :$

$$G_{55} = \mu_x M_\beta + \mu_y$$

$$G_{56} = -\mu_x \frac{M_\beta K}{S_\alpha}$$

$$G_{66} = \mu_x \frac{M_\beta K}{S_\alpha^2} + \mu_y + \mu_z \frac{d^2}{D^2} \frac{M_\beta}{S_\alpha^2}$$

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BOOK REVIEWS

THE CHEMISTRY OF NATURAL PRODUCTS, Edited by K. W. Bently, Volume I. "The Alkaloids" by K. W. Bently. Interscience Publishers, New York. 1957. pp. 237.

The "Alkaloids" is the first of a series to be published and this is expected to have a wide coverage on the chemistry of natural products. In fact during the last three years a few volumes have already appeared. The aim of these publications as stated in the "Introduction" particularly the present one, is to have a golden mean between exhaustive treatises like "The Alkaloids" edited by Manske and Holmes and "The Plant Alkaloids" by Henry, primarily meant for the benefit of graduate students in British Universities.

It becomes extremely difficult for the author, who has however made notable contributions towards our knowledge of alkaloids, to apply his discretion with judgment consistent with clarity of expression, when he has to deal with an already vast and a rapidly expanding subject in such a short span of about 225 pages. Naturally many important topics of current interest had to be omitted in this book. Particular mention may be made of the absence of any chapter on Rauwolfia and curare alkaloids. Another aspect which merits considerable attention is that sufficient emphasis has been placed on biogenesis for better understanding of the formation of and correlation amongst different groups of alkaloids. It may be mentioned that these half-tested truths and plausible assumptions are now-a-days being accepted as absolutes and realities and this shows some unscientific tender-mindedness on the part of some authors.

Coverage of the book is quite commendable and it is a pleasant reading because of profusely neat and hand-drawn structures in every alternate page of the book. The only criticism that can be made is that some errors have crept into the book, which are, of course, trivial in nature. Lot of credit goes to the author in presenting this volume at such a low price thereby making it available to a wide circle of readers and from these considerations, purpose of writing this book has been fully justified.

P. C. D.

PRINCIPLES OF PHYSICAL SCIENCE—By F. T. Bonner and M. Phillips, August, 1957, pp. 716, Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, U.S.A. Price \$ 7.50.

It is now a well recognised fact that science has become such an integral part of our life that a basic knowledge of it is essential even for persons who are not

directly connected with science. It is a difficult task to give in the compass of a single volume the fundamentals of the physical sciences in a form which can be understood by the readers having no scientific background. In the present book the authors have performed this task very creditably. They have been able to give a coherent picture of the physical sciences from the astronomy of ancient Greeks to the modern chemistry, nuclear physics, geophysics etc. The topics for discussion have been very carefully chosen from the different branches of science so as to represent a good overall picture. The treatment of the various scientific phenomena is very clear and interesting. A large number of carefully designed illustrations is given which makes it easier to grasp the fundamentals. The book may be useful to fresh college students of science as additional reading. The large number of instructive examples at the end of each chapter will help to clarify the physical ideas. The get-up of the book is excellent.

B.N.S.

PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON ISOTOPE SEPARATION", edited by Kistemaker, Bigeleisen and Nier. (North-Holland Publishing Co.)

This volume is a compilation of the papers read at the first international symposium on isotope separation held in Amsterdam in 1957, organised by the Netherlands Physical Society in collaboration with the International Union of Pure and Applied Physics. There are at present not many standard books on the theory and method of isotope separation. The publication of this volume giving the latest achievements in this field is most welcome.

The study of the science of isotope separation has received great impetus during the last two decades with the discovery of nuclear fission and the use of separated isotopes as a tool for investigation of problems in chemistry, physics, biology and production technology. The book deals with both the science and the technology of production of isotopes, their purification and properties and covers a wide ground. All the papers are conveniently grouped according to the method of separation employed, under the following nine parts :

1) Chemical Engineering, 2) Molecular Interactions, (3) Chemical Exchange, 4) Electromigration, 5) Distillation, 6) Thermal Diffusion, 7) Diffusion, 8) Electromagnetic Separation, 9) Ultra-centrifuges.

The chemical engineering section deals mainly with the design procedure for large scale isotope separation units starting from basic laboratory data while the second section deals with the physical properties of isotope mixtures whose knowledge is essential for the understanding of the different processes. In the section on "Diffusion" also various aspects of design theory for large diffusion

plants have been discussed. Reports on plants for large scale separation of nitrogen, hydrogen and boron isotopes as well as discussions on the theory of the process of isotope separation by chemical exchange have been included under the section "Chemical Exchange", while separation of isotopes of oxygen, lithium, hydrogen and boron by distillation process, and the economic considerations of a fractional distillation plant have been presented in "Distillation" section. The theory and performance of multi-stage thermal diffusion columns, have been discussed in the section on "Thermal Diffusion" and the production of U^{235} for the Manhattan District programme has been described. The operational experience of electromagnetic separators in Harwell and Oak-ridge has been described in the section on "Electromagnetic Separation". The progress in the practical aspects of isotope separation by the two comparatively new methods of electromigration and gas centrifuge has been reported in another two sections.

From the brief resume of the different sections given above it will be clear that the papers presented at the symposium cover a very wide spectrum of methods now available for isotope separation. The book will be very useful to all those who have some acquaintance with the subject and want to keep themselves abreast of the existing literature and the present trends. Sufficient details about design and construction have been given at several places to make the study more useful and realistic. The editors and the publishers are to be thanked for providing such a collection of up-to-date information about this very modern and developing subject.

B. N. S.

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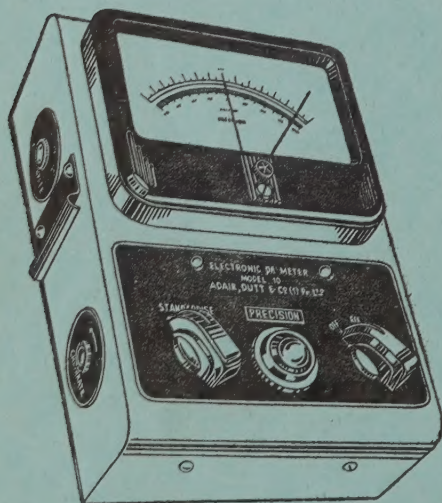
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